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AUTHOR(S):

Mukoyama, Takeshi; Adachi, Hirohiko

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Slater Transition-State Calculation of One-Photon-Two-Electron Excitation Energies

Takeshi MUKOYAMA and Hirohiko ADACHI

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The relativistic Hartree-Fock-Slater transition-state method is used to calculate the energies of the one-photon-two-electron excitation in the X-ray absorption spectra. The numerical results are in good agreement with the measured values and with the conventional relativistic Hartree-Fock-Slater calculations. The difference in the physical meaning between the present method and the conventional one is discussed.

KEY WORDS: Relativistic Hartree-Fock-Slater Method/ Transition State/
One-Photon-Two-Electron Excitation Energy/

I. INTRODUCTION

A multielectron transition in atoms has been known since early days of X-ray spectroscopy, but recently received special attention with the advent of high-energy-resolution X-ray detectors. One-photon-two-electron excitation is one of such multielectron transition processes in which two electrons in the same atom are excited by absorption of a single photon. The first experimental evidence for this process was observed in the absorption spectrum of He gas by Madden and Codling.¹⁾ More recently Salem *et al.* reported a series of experimental results on this process for germanium,²⁾ zinc,³⁾ and praseodymium and samarium.⁴⁾ They observed discontinuities in the X-ray absorption spectra of these elements at the points corresponding to the energies for simultaneous excitation of two electrons. The observed energies were found to be in agreement with the calculations based on the relativistic Hartree-Fock-Slater model (RHFS).

It is well known that in the RHFS the energy eigenvalues agree neither with those of more realistic theoretical models, such as the relativistic Hartree-Fock model, nor with the experimental binding energies.⁵⁾ However, in the case of relative energy, such as the energy shift of X-ray satellite spectra induced by ion-atom collisions, the systematic deviations of RHFS calculations from the experimental binding energies tend to cancel out and the agreement between the RHFS and the experimental values is good.⁶⁾ This may be the reason for good agreement between the calculated and measured values of Salem *et al.* described above.

On the other hand, Slater *et al.*⁷⁻⁹⁾ have shown that when the Slater's statistical approximaton is introduced for the electron exchange term, the energy eigenvalues have the different physical meaning from that of the Hartree-Fock (HF) model. In the

向山 毅: Laboratory of Nuclear Radiation, Institute for Chemical Research, Kyoto University, Kyoto 606.

足立裕彦: Hyogo University of Teacher Education, Shimokume, Yashiro-cho, Kato-gun, Hyogo 673-14.

Slater approximation, the eigenvalues are partial derivatives of the total energy with respect to the orbital occupation numbers. This fact means that the Koopmans' theorem does not valid and the X -ray transition energy cannot be determined directly from the difference between two energy eigenvalues. Instead, Slater⁹⁾ proposed a concept of transition state in which the electron having a transition stays half in the initial state and half in the final state. Then the transition energy can be given as the difference between two energy eigenvalues of the atomic orbitals concerned.

The Slater's transition-state idea has been widely used in atomic and molecular physics and successfully applied to the calculations of ionization energies,^{10,11)} This method has been also shown to be useful to estimate the transition energies of multielectron processes, such as two-electron-one-photon process,¹²⁾ the X -ray photoelectron shake-up process,^{13,14)} and the KLL Auger effect.¹⁵⁾ For these processes, the Slater transition-state model gives energies in good agreement with the HF model and even closer to the experimental values than the latter model. However, all these calculations are nonrelativistic and no attempt has been reported to incorporate the transition-state concept into the RHFS model. In the present work, the one-photon-two-electron excitation energies have been calculated with the RHFS by the use of the Slater transition-state model and the results are compared with the experimental data of Salem *et al.* as well as with the conventional RHFS calculations.

II. METHOD

The calculations have been made using the RHFS program,¹⁶⁾ which is equivalent to the computer program of Liberman, Cromer, and Waber.¹⁷⁾ The exchange potential is given by

$$V_{ex}(r) = -1.5\alpha e^2(3\rho(r)/\pi)^{1/3}, \quad (1)$$

where e is the electric charge, α is the exchange scaling parameter and $\rho(r)$ is the electron density at the position r . The parameter α was often taken to be unity,¹⁸⁾ but

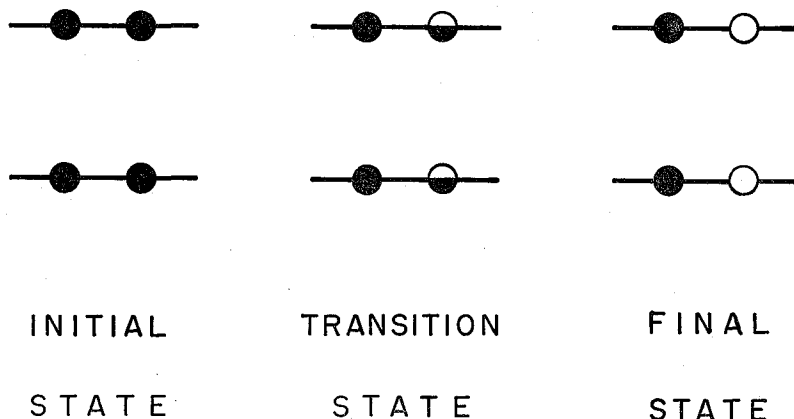


Fig. 1. Schematic drawings of initial state, transition state, and final state in the one-photon-two-electron excitation process. The solid circles indicate the electron and the open circles represent the vacancy. In the transition state, the fractional number of the electron (the vacancy) is used.

the optimum value may be smaller for medium and heavy elements. Following the nonrelativistic results of Schwarz,¹⁹⁾ the value of $\alpha=0.7$ has been used throughout the present work without Latter tail correction.²⁰⁾

The effect of the finite nuclear radius is taken into account by assuming the nucleus as a uniformly charged sphere. In this approximation the potential inside the nucleus is expressed by

$$V(r) = -\frac{Ze^2}{2R}[3 - (r/R)]^2, \quad (2)$$

where Z is the atomic number and R is the nuclear radius.

In the transition-state method, the electrons involved in the transition are considered to stay half in the initial state and half in the final state. Figure 1 shows the initial, final and transition states for the one-photon-two-electron transition schematically. The solid circles indicate the electron, while the open circles represent the vacancy. The RHFS calculations have been made for the atomic configuration in the transition state.

III. RESULTS AND DISCUSSION

In Table I, the ionization potentials calculated by the transition-state method are compared with the energy eigenvalues of the Dirac-Fock (DF) model²¹⁾ and with the observed values.²²⁾ According to the Koopmans' theorem,²³⁾ the DF energy eigenvalues can be considered as the ionization potentials. On the other hand, in the transition-state method the ionization potential is obtained by the energy eigenvalue for the electron configuration in which one-half of an electron is removed from the atomic shell concerned. It is clear from the table that the transition-state method gives the ionization potential in good agreement with the observed value. Agreement is better than for the case of the DF values based on the Koopmans' theorem.

It is convenient to express the one-photon-two-electron excitation energy as the

Table I. Comparison of the calculated and observed ionization potentials (in eV).

Element	Shell	Calculated value DF ^a	Present ^b	Observed value ^c
Zn	K	9735	9689	9658.6±0.6
	L ₁	1234	1182	1193.6±0.9
	L ₂	1081	1052	1042.8±0.6
	L ₃	1057	1027	1019.7±0.6
Pr	L ₁	6903	6799	6834.8±0.5
	L ₂	6507	6454	6440.4±0.5
	L ₃	6023	5963	5964.3±0.4
Sm	L ₁	7812	7693	7736.8±0.5
	L ₂	7386	7322	7311.8±0.4
	L ₃	6781	6709	6716.2±0.5

^a Dirac-Fock method taken from Desclaux (Ref. 21).

^b RHFS transition-state method.

^c Taken from Bearden and Burr (Ref. 22).

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Table II. Comparison of the difference between the energy required for the two-electron simultaneous excitation and the sum of the energies for their single excitation (in eV).

Transition	Element	Calculated Conventional ^a	Present	Experimental	Ref.
$E(1s^{-1} + 2s^{-1}) - [E(1s^{-1}) + E(2s^{-1})]$	Zn	86	86.1	94.4 ± 5.0	3
$E(1s^{-1} + 2p_{1/2}^{-1}) - [E(1s^{-1}) + E(2p_{1/2}^{-1})]$	Zn	104	103.2	114.20 ± 5.0	3
$E(1s^{-1} + 2p_{3/2}^{-1}) - [E(1s^{-1}) + E(2p_{3/2}^{-1})]$	Zn	102	100.6	112.70 ± 5.0	3
$E(2s^{-1} + 2p_{1/2}^{-1}) - [E(2s^{-1}) + E(2p_{1/2}^{-1})]$	Pr	163	165.2	162.50 ± 10	4
$E(2s^{-1} + 2p_{3/2}^{-1}) - [E(2s^{-1}) + E(2p_{3/2}^{-1})]$	Pr	157	159.2	168.60 ± 10	4
$E(2p_{1/2}^{-1} + 2p_{3/2}^{-1}) - [E(2p_{1/2}^{-1}) + E(2p_{3/2}^{-1})]$	Pr	178	180.3	191.20 ± 10	4
$E(2s^{-1} + 2p_{1/2}^{-1}) - [E(2s^{-1}) + E(2p_{1/2}^{-1})]$	Sm	172	173.2	176.50 ± 10	4
$E(2s^{-1} + 2p_{3/2}^{-1}) - [E(2s^{-1}) + E(2p_{3/2}^{-1})]$	Sm	165	166.0	190.40 ± 10	4
$E(2p_{1/2}^{-1} + 2p_{3/2}^{-1}) - [E(2p_{1/2}^{-1}) + E(2p_{3/2}^{-1})]$	Sm	187	188.8	183.80 ± 10	4

^a Taken from Refs. 3 and 4.

difference from the sum of the single excitation energies of the individual electrons. Table II shows the comparison of the one-photon-two-electron excitation energies calculated in the transition-state method with those due to the conventional RHFS calculations and with the experimental results of Salem *et al.*^{3,4)} The conventional RHFS values are taken from Refs. 3 and 4. In this case, the difference between the energies for the simultaneous excitation of the i - and j -shell electrons and for the independent excitation of these electrons is given by

$$\Delta_{ij} = E_j(i) - E_j(\text{ground}), \quad (3)$$

where $E_j(i)$ is the energy eigenvalue of the j -shell electron with the presence of the i -shell vacancy and $E_j(\text{ground})$ is that of the j -shell electron in the ground state. Nothing has been written in the papers of Salem *et al.*^{3,4)} about what value α they used, but when we choose $\alpha=1$, we can obtain the values cited in the table by the use of our computer code.

In the case of the transition-state method, the energy difference is expressed as

$$\Delta_{ij} = E_i^{TS}(i+j) + E_j^{TS}(i+j) - E_i^{TS}(i) - E_j^{TS}(j), \quad (4)$$

where $E_i^{TS}(i+j)$ is the energy eigenvalue of the i -shell electron corresponding to the transition state for simultaneous excitation of the i - and j -shell electrons and $E_i^{TS}(i)$ is that corresponding to the transition state for the single i -shell excitation.

It can be seen from the table that the values calculated by the transition-state method are in very good agreement with those in the conventional RHFS method and that both calculated values agree well with the experimental values. It should be noted, however, that although agreement between the transition-state method and the conventional method is very good, the physical meaning of the energy difference in these two methods is quite different. As can be seen from Eq. (3), the calculation of the energy shift in the conventional method is based on the assumption that the one-photon-two-electron excitation takes place as a two-step process; first the i -shell electron is excited and in the second step the j -shell excitation occurs for an atom having an i -shell va-

cancy. The energy difference between the two-electron excitation and two independent single excitations arises from the difference in the single electron energy eigenvalues with and without an inner-shell vacancy.

On the other hand, Eq. (4) means the simultaneous excitation of two electrons and in the transition-state method the one-photon-two-electron excitation is considered as a one-step process. The energy shift for the two-electron excitation comes from the sum of the differences of the energy eigenvalues of each electron. It has been well established that the multielectron transition should be treated as a one-step process. Therefore the transition-state method is more realistic than the conventional method. Furthermore, in the transition-state method the energy eigenvalue, $E_i^{TS}(i)$, is in good agreement with the measured ionization potential as shown in Table I, while agreement between the energy eigenvalue $E_i(\text{ground})$ in Eq. (3) in the conventional method and the experimental value is poor.

In conclusion, the transition-state method used in the RHFS model can reproduce the experimental one-photon-two-electron excitation energies with very good accuracy. Although the conventional RHFS method also gives the result in good agreement with the RHFS transition-state method, the physical meaning of the energy shifts in these two methods is quite different. In the conventional method, the energy shift is estimated under the assumption of the two-step model and the calculated ionization potentials for the single excitation are in poorer agreement with the observed values. Considering these facts, the transition-state method is better to describe the one-photon-two-electron excitation process.

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